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Published in:
Procedings of 2. World Conference and Technology Exhibition on Biomass for Energy and Industry

Publication date:
2004

Document Version
Early version, also known as pre-print

Link back to DTU Orbit

Citation (APA):
Ahrenfeldt, J., Jensen, T. K., Henriksen, U. B., Gøbel, B., & Schramm, J. (2004). CO Emissions from Gas Engines Operating on Biomass Producer Gas. In W. P. M. van Swaaij, T. Fjällström, P. Helm, & A. Grassi (Eds.), *Procedings of 2. World Conference and Technology Exhibition on Biomass for Energy and Industry*

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CO Emissions from Gas Engines Operating on Biomass Producer Gas

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ABSTRACT High carbon monoxide (CO) emission from gas engines fueled by producer gas is a concerning problem in the struggle to make biomass gasification for heat and power production a success. CO emissions from engines operating on biomass producer gases are high, especially at very lean conditions where the emissions exceed the regulated limit significantly. The high CO emissions are mainly due to the high content of CO in the fuel and can – in origin – be compared with the emission of unburned hydrocarbons (UHC) from natural gas engines, thus CO emissions from producer gas engines are a measure of fuel passing unburned through the combustion. Measurements of the slip of the producer gas fuel components CO and CH_4 showed that these are of similar order. When the environmental effect of the emissions is discussed, unburned hydrocarbons in the form of methane is a strong greenhouse gas (21 times higher than CO2) while CO only indirectly through photochemical reactions is involved in the production of the greenhouse gas ozone.
Keywords: Gas engines, CO emissions, PAH,

1 CO REGULATIONS

1.1 Background

Regulations for CO emissions have been applied for solid fuel fired power plants for many years. The argument for regulating the CO emission has been that a high CO emission is a measure for incomplete combustion of hydrocarbons and thus an indicator for the presents of organic micro emissions such as polynuclear aromatic hydrocarbons (PAH). Formation of CO emissions from combustion of solid organic fuel are due to incomplete combustion of hydrocarbons, meaning that the terminating reaction (see Reaction 1) in the hydrocarbon oxidation scheme does not take place due to lack of oxidiser. PAH emissions on the other hand are products of pyrolysis of hydrocarbons, hence it is possible to have PAH formation without any CO being formed. The assumption that there is a correlation between CO and PAH emissions origins from combustion of solid fuels in boilers and furnaces. CO emissions from a boiler will be high if the bulk λ value is below 1 (see Equation 1 for definition of λ) meaning insufficient oxygen for complete combustion of the fuel, or if – due to pour mixing – there are local spots with λ<1. If there is a lack of oxygen in local spots in the boiler pyrolysis of the fuel take place instead of combustion and PAH may be formed. If temperatures in the boiler are high the PAH may crack or decompose.

Correlation between CO and PAH from combustion of solid fuels have been shown in several investigations [1,2,3]. Good correlation between CO and PAH were shown for a fixed temperature of 1000 ^oC and decreasing λ. At lean combustion λ>1 CO and PAH emissions were low and at λ<1 CO and PAH emissions were high. At a temperature of 1300 ^oC PAH diminishes by an order of magnitude for all values of λ, while CO levels are increasing, this shows that at elevated boiler temperatures, high CO emissions may not be an adequate indicator for PAH emissions [1].

1.2 Current regulations

The origin of CO emission from engines operating on biomass producer gas is fundamentally different from CO emissions from engines operating on natural gas as will be described in the following sections. This is not taking into account by the present regulations, which are—based on natural gas—so low that no plant could uphold regulations without expensive equipment for after treatment of the emissions. Separate regulations will have to be applied for engines operating on biomass producer gas. Table 1 shows the CO emission limits from different European countries for engines operated on producer gas.

Table 1 CO emission regulations for new engines operating on producer gas in different countries.

Country	CO [mg/m^3_n]	Capacity [MW_{th}]	Ref. [Vol.%O_2]
Denmark[4]	500	0.12-5	5
Germany[5]	300	All	5
Holland [6]	250	1.5-5	11
Switzerland[1][6]	650	-	5
Italy[1][6]	800	0-3	5
Italy[1][6]	650	>3	5
Portugal[6]	1000	-	-
Greece[2][6]	-	-	-
France[3][6]	-	-	-
Spain[6]	625	-	-
Belgium[4][5]	300	All	5

[1]National levels, levels can be lowered regionally. [2]Limited emission concentration in the atmosphere at a specific location, regardless the source. For CO, this limit is 10 mg/m3 in 8 hour basis. [3] The regulations for natural gas combustion is 650 mg/m^3_n@5%O_2. [4]The regulation used in Belgium for emissions is the German TA Luft [5,6].

2 THEORY

The CO present in producer gas originates from the biomass used as fuel for the gasification process. The process can largely be divided into three steps, pyrolysis, oxidation and char gasification. The formation of CO from gasification of biomass depends on the water content, the amount of air/oxygen added to the process, oxidation temperature and the degree of char conversion.

2.1 CO Emissions

CO emission from spark ignition (SI) engines fueled by hydrocarbon fuels is controlled primarily by the air-fuel ratio (A/F) [7]. To describe engine operation in terms of the air-fuel ratio the term excess of air or specific air-fuel ratio (λ) is used, the term is defined by the ratio of the actual air-fuel ratio and the stoiciometric air-fuel ratio.

$$\lambda = \frac{A/F_{Actual}}{A/F_{Stocio.}} \qquad \textbf{Equation 1}$$

Natural Gas

For fuel-rich operation (λ<1.2) CO emissions increase significantly with decreasing λ, this is due to partial oxidation of hydrocarbons, meaning that Reaction 1 is limited by the lack of oxygen.

At conditions leaner than λ>1.2 the CO emissions increase again. The CO formation during lean conditions is also caused by partial oxidation of hydrocarbons but the governing factor here is not lack of oxygen. At lean conditions the temperature at the end of the combustion cycle can get so low that Reaction 1 stops and this results in high CO emission.

$$CO + OH \rightarrow CO_2 + H \qquad \textbf{Reaction 1}$$

Producer Gas

CO emissions from engines operating on producer gases are high, especially at very lean conditions (λ>1.5) where the emissions extend the regulated limits significantly. As producer gases only contain small amounts of hydrocarbons (see Table 5) it is not likely that the high emission of CO can origin from incomplete combustion of hydrocarbons. The main contributor is the emission of unburned fuel-CO (UCO).

When operating an engine very lean a governing factor concerning emission of unburned fuel is bulk quenching. This means that the flame extinguishes in the bulk gas before the combustion is completed [7]. Since producer gases only contain a minor amount of methane the emission of UHC from lean combustion is not significant (see Figure 1). The CO content of producer gas on the other hand is 15-35% on a dry volume basis. This means that the major unburned emission from producer gas combustion will be CO. Another factor is fuel being trapped in crevices in the combustion chamber were the propagating flame cannot penetrate into during the combustion process. The fuel trapped in the crevices will flow back into the combustion chamber during the expansion stroke where it will be oxidised if there is an excess of air in the chamber [8]. This occurs though at low temperature where the combustion efficiency is low and thus some fuel-CO will escape this post oxidation unburned.

2.2 PAH Emissions

Formation of PAH in a gas engines can origin from several sources:

- Organic aerosols.
- Higher hydrocarbons in the fuel gas.
- Engine lubricant.

Several factors control the formation of PAH. If the engine is running fuel-rich (λ<1) aerosols and gaseous higher hydrocarbons are not oxidised completely but pyrolysed instead and tars and PAH can be formed. A second factor is the fuel trapped in crevices in the combustion chamber. If the fuel flowing out from the crevices only sees hot exhaust gas, pyrolysis of the fuel can occur and PAH can be formed.

A third factor contributing to PAH formation is partly combustion/pyrolysis of lubricants from the cylinder walls, this happens when the hot flame reaches the cylinder walls during the combustion process.

Since all modern stationary gas engines are lean burn engines, formation of PAH is not likely to take place in these engines. Measurements made in Denmark on stationary gas engine power plants operating on both biogas and natural gas confirms this. The measurements showed emissions 70-200 times lower than the recommended limit in Denmark [9]. CO emissions for the same engines were ranging from 300 to 660 mg/m^3_n@5% O_2. These measurements imply that even for hydrocarbon containing gaseous fuels high CO emissions is not an adequate indicator for PAH.

3 MEASURMENTS

Measurements from three operating gasification plants equipped with gas engines are presented.

The Viking Plant: Technical University of Denmark. The plant is a test-plant that has been running for more than 1900 hours of engine operation since 2002.
The Güssing Plant: Güssing, Austria. The plant is a full scale operating CHP demonstration plant. The engine has been operating for more than 5000 hours since 2002.
The Harboøre Plant: Harboøre, Denmark. The plant is a full scale CHP demonstration plant. The two engines have been operating continuously since 2000.

The plants represent three fundamentally different gasification concepts and give a good picture of the diversity of biomass gasification. The engines from the Güssing and the Harboøre plants are new large-scale gas engines from Jenbacher while the engine from the Viking plant is an older Deutz-MWM gas engine.

Table 2 to Table 4 shows the specifications of the three plants and Table 5 shows examples of gas compositions.

As it seen from Table 5 the gas compositions from the different gasifiers vary significantly, the CO content for example varies from 18 vol.% to 29 vol.%. The variations in gas composition give rice to a variation in the emission of unburned fuel from the different engines.

Table 2 Data from the Viking plant.

Gasification concepts	Two-stage
Thermal input [kW]	68
Fuel [-]	Wood chips
Electric output [kW]	18
Operating λ [-]	1.4-1.8
Engine electric efficiency [%]	27
Overall electric efficiency [%]	25

Table 3 Data from the Güssing plant.

Gasification concepts	Fast internally CFB
Thermal input [MW]	8
Fuel [-]	Wood chips
Electric output [MW]	1.5
Operating λ [-]	2.2-2.4
Engine electric efficiency [%]	39
Overall electric efficiency [%]	25

Table 4 Data from the Harboøre plant.

Gasification concepts	Up-draft
Thermal input [MW]	5
Fuel [-]	Wood chips
Electric output (2 engines) [kW]	768+648
Operating λ [-]	2.2-2.4
Engine electric efficiency [%]	40
Overall electric efficiency [%]	28

Table 5 Gas compositions from the different plants.

Component	Viking	Güssing	Harboøre
H_2	31	35	19
CO	18	29	23
CO_2	15	16	12
CH_4	1	9	5
H_20	dry	6	dry
N_2	35	3	41
C_2H_6	-	2	-

Figure 1 shows measurements, made at the Viking plant, of the CO and UHC emissions from the engine.

The emissions are depicted as one-hour average values from two days measurements. It is seen that the CO emission is significantly higher than the UHC emissions –28 times on ppm basis–, this corresponds well to the difference between the CO and CH_4 content of the producer gas –there is 18 times more CO than CH_4 in the gas.

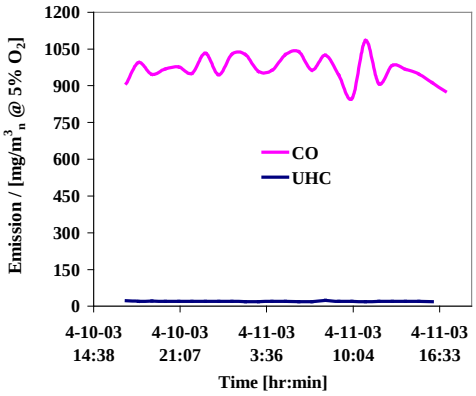

Figure 1 CO and UHC emissions from the Viking plant, λ=1.4.

The emission of hydrocarbons is as described earlier an emission of unburned fuel (UHC), if, as stated, the emission of CO also is an emission of unburned fuel then the slip of CO and CH_4 should be of the same order. The slip of fuel is calculated as the following.

$$Slip = \frac{\dot{n}_{CO\_out}}{\dot{n}_{CO\_in}} \cdot 100\% \qquad \text{Equation 2}$$

Figure 2 shows the slip of CO and CH_4 from the engine at the Viking plant. The slip of CO and CH_4 are, as stated, of the same order of magnitude, the slight advance in slip of CO is expected since CO is a more stable molecule than CH_4, also a small fraction of the CO emission may origin from partial oxidation of CH_4. This validates that the emission of CO from the engine is an emission of unburned fuel-CO.

Table 6 shows the CO emission from the engines at the three plants. It is seen that the emission from the Viking engine is significantly lower than the other two, this is because the Viking engine is operated at lower λ-value than the other two. The engine at the Güssing plant has the highest CO emission of the three engines corresponding to the high CO content of producer gas from the plant. At the Harboøre plant tests have been made with catalytic reduction of the CO emission, the tests showed an average reduction of 76% but even though the reduced emission was still higher than the regulated limit in Denmark.

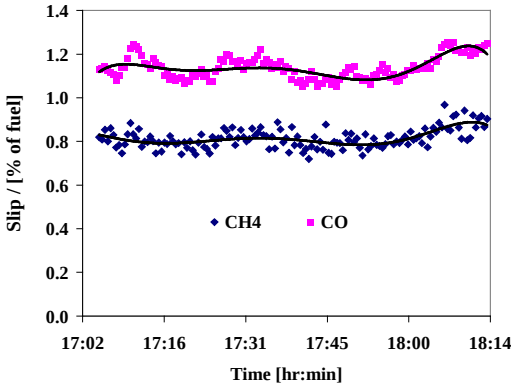

Figure 2 The percentage of the fuel components CO and CH_4 that passes unburned through the engine, λ=1.4.

Table 6 The CO emissions from the three plants [10,12].

Plant	λ [-]	CO emission [mg/m^3_n @ 5% O_2]
Viking	1.2-1.8	670-1850
Güssing	2.2-2.4	2000-4500
Harboøre	2.2-2.4	1800-3100

Table 7 shows the benzo[a]pyrene-equivalent PAH emission from the Viking plant and the Harboøre plant. The measurement from the Viking plant was made parallel with the CO emissions shown in Figure 1. It was not possible to detect any PAH components for the measurements form the Viking plant. Because the analysis were carried out with a fairly high detection limit, the given value for the PAH emission is a worst-case value calculated from the detection limits for each component. It could be concluded that the emission from the engine was below 1.95 $\mu g/m^3_n$. This is several times below the regulated value of 5 $\mu g/m^3_n$ [11] thus showing that the high CO emission is not corresponding to high PAH emissions.

Table 7 PAH emissions from the Viking plant and the Harboøre heat and power plant. [12].

benzo(a)pyrene-equivalent @ 5% O_2	[$\mu g/m^3_n$, dry]
Viking	<1.95
Harboøre	0.23

The measurements from the Harboøre plant show that the emission of PAH is very low, about 22 times lower than the recommended benzo[a]pyrene-equivalent PAH emission limit in Denmark. Many components were not detected in the analysis because the concentrations were below the detection limit for the analysis, so again here the given value for the benzo[a]pyrene-equivalent PAH emission is a worst case value. The very low PAH emission is corresponding to a high CO emission as described above. This validates again that high CO emissions do not result in high PAH emissions for engines fueled by producer gas.

4 CO AND GLOBAL WARMING

Carbon monoxide is not a greenhouse gas in it-self, but indirectly it has an effect on global warming by elevating the concentration of CH_4 and ozone in the troposphere [13]. By chemical reactions CO reduces the concentration of the hydroxyl radical (OH) that would otherwise participate in the destruction of CH_4 and ozone. The destruction of CO may both lead to formation or destruction of ozone. Carbon monoxide concentrations

are though short-lived in the atmosphere and are spatially variable. The initiating reaction for CO destruction is:

$CO+OH \Rightarrow CO_2+H$ **Reaction 2**

In the presence of high NO_x concentrations CO leads to photochemical production of ozone [13].

$CO+2O2+hv \Rightarrow CO2+O3$ **Reaction 3**

For low NO_x concentrations CO leads to ozone destruction [13].

$CO+O_3 \Rightarrow CO_2+O_2$ **Reaction 4**

Since CO has an indirect effect on global warming it is difficult to asses the global warming potential of the emission. CO is reported to have a GWP between 3.2 [14] and 4.5 [15] on a 20 years time span and 1.2 [14] on a 100 years time span. In comparison CH4 has a GWP of 56 on a 20 years time span and 23 on a 100 years time span [16]. Given the assumption that electricity produced by biomass gasification replaces electricity from coal or natural gas, the application of producer gas will decrease the overall emission of CH_4 significantly. The emission of CH_4 from engines operating on producer gas is 20-50 mg/m^3_n@5% O_2 while for engines operating on natural gas the emission are 1000-1500 mg/m^3_n@5% O_2, this means a reduction in CH_4 emissions of 30 times. Assuming that the average emission of CO from engines operating on producer gas is 2000 mg/m^3_n@5% O_2 this still would give a reduction in GWP of more than 85% compared to natural gas.

5 DISCUSSION AND CONCLUSION

The high CO emissions from engines operating on biomass producer gases are mainly due to the high content of CO in the fuel and are therefore, like UHC emissions from natural gas engines, a measure of fuel passing unburned through the combustion. The comparison ends though when the environmental effect of the emissions is discussed, where unburned hydrocarbons in the form of methane is a strong greenhouse gas (21 times higher than CO_2) CO is only indirectly involved through photochemical production of the greenhouse gas ozone [13].

The assumption regarding CO being an indicator for PAH emissions has been adopted from regulations concerning solid fuel firing when regulations for gas engines were prepared. Measurement showed that there is no relation between a high CO emission and high PAH emission for engines operating on biomass producer gas. Measurements of PAH emissions equivalent to a CO emission of 2800 mg/m^3_n@5% O_2 were about 22 times lower than the recommended emission limit in Denmark, verifying that CO emission is not an adequate indicator for PAH emissions.

Since the origin of CO emissions from biomass producer gas is fundamentally different than CO emissions from both natural gas and biogas, separate regulations will have to be applied for engines operating on biomass producer gas. A regulated limit for CO emissions of 2000 mg/m^3_n@5% O_2 would be realistic and appropriate.

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